PATENT ABSTRACTS OF JAPAN

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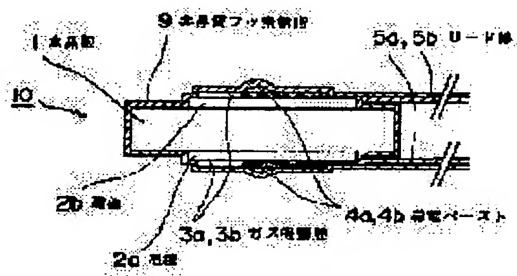
(54) SULFUR HEXAFLUORIDE DECOMPOSED GAS SENSOR

(57)Abstract:
PURPOSE: To provide an SF6 decomposed gas sensor having little sensitivity deterioration.
CONSTITUTION: SF6 decomposed gas adsorption films 3a, 3b are formed on the mass load sensitive faces of a mass load sensitive vibrator, and the SF6 decomposed gas adsorption films 3a, 3b or preferably the whole mass load sensitive vibrator including the SF6 decomposed gas adsorption films 3a, 3b is covered with fluororesin 9. A sensor having little sensitivity deterioration on the SF6 gas and the SF6 cracked gas can be realized, and the SF6 decomposed gas in an SF6 gas-sealed electric apparatus can be continuously detected at high sensitivity over a long period with it.



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CLAIMS

[Claim(s)]
[Claim 1] It is [the 6 fluoride sulfur-content solution gas-adsorption film of the mass load induction vibrator from which it sympathizes with change of a mass load, and the electrical property changes formed in the mass load induction side at least, and] the above SF 6 at least. Vibrator type 6 fluoride [sulfur] solution gas sensor which possesses the fluororesin layer which covers a cracked gas adsorption film, and is characterized by the bird clapper.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention is vibrator type SF6 for detecting the cracked gas of the 6 sulfur fluoride (SF6) enclosed with the electrical machinery and apparatus for high voltages as insulating gas. It is related with a decomposition gas sensor.
[0002]
[Description of the Prior Art] Generally it is SF6 as insulating gas of the electrical machinery and apparatus which deals with the high voltage and high current. It is used. This is SF6. It is the thing which gas has and to depend on thermal and chemical stability. however, SF6 if oxygen and moisture exist in the interior of the enclosed electrical machinery and apparatus and corona discharge and arc discharge happen -- mediation of these oxygen or moisture -- SOF2 and SO two F2 etc. -- SF6, such as low-grade sulfur fluoride gas and HF gas, Cracked gas is produced. These cracked gas is acid corrosion gas, and since it causes [of an electrical machinery and apparatus] an insulating fall, it needs to detect the abnormalities of insulating gas in a low-concentration stage. For this reason, for example in the gas insulated switchgear (it is hereafter called GIS for short), the method (refer to 33rd volume No. 4 and SF6 insulation device maintenance manual of research common [electric]) using a gas chromatograph, the gas checker (Mitsubishi Electric technical report Vol.60, No6-1986) using the color reaction reagent, etc. are used. However, since it is the work which requires time and effort and time extremely, the measurement using equipments, such as this, is SF6. Development of the sensor in which continuation detection is possible at the high sensitivity for automating detection of cracked gas is desired.
[0003] On the other hand, many sensors to which the mass load effect of a quartz resonator was applied by high sensitivity in the field of a gas sensor as a gas sensor in which a room temperature drive is possible in recent years are tried. This sensor has structure which generally formed the gas-adsorption film on the electrode of a quartz resonator (mass load induction side), and the amount of gas can be detected by measuring oscillation frequency change deltaf of the quartz resonator to which weight change deltaw of a gas-adsorption film based on adsorption of gas is given by principle formula like the following formula (1).
deltaf=-2.3x106 xf2 xdeltaw/A (1)
Here, f is the oscillation frequency of a quartz resonator and A is the electrode area of a quartz resonator.
[0004] SF6 The place which examined various cracked gas adsorption material based on the quartz-resonator type gas sensor as a decomposition gas sensor, A triethanolamine, a KUADO roll, tetrahydro KISHIE chill ethylenediamine, etc. solve, and a polar big organic material is SF6. Although it found out that high sensitivity was shown in cracked gas It is SF6 about the sensor which formed such material as a gas-adsorption film. The oscillation frequency of the sensor left in gas has the inclination fallen and stabilized with time. It follows on this and is SF6. Although short-term neglect shows sensitivity in first stage, it is almost lost soon, and cracked gas sensitivity is SF6. After stabilizing by neglect among gas, there was a trouble that sensitivity was hardly shown.
[0005]
[Problem(s) to be Solved by the Invention] It is made in view of the above-mentioned situation, and this invention is SF6. About cracked gas, they are high sensitivity and continuously detectable SF6. It aims at offering a decomposition gas sensor.
[0006]
[Means for Solving the Problem] in order to solve the above-mentioned technical problem to this invention -- the mass load induction side of mass load induction vibrator -- SF6 while forming a cracked gas adsorption film -- at least -- the above SF 6 a cracked gas adsorption film -- desirable -- the above SF 6

It is characterized by providing the means of a wrap for the whole mass load induction vibrator containing a cracked gas adsorption film by the fluororesin.

[0007] That is, this invention is SF6 of the mass load induction vibrator from which it sympathizes with change of a mass load, and the electrical property changes formed in the mass load induction side at least. It is [a cracked gas adsorption film and] the above SF 6 at least. Vibrator type SF6 which possesses the fluororesin layer which covers a cracked gas adsorption film, and is characterized by the bird clapper A decomposition gas sensor is offered.

[0008]

[Function] at least -- the above SF 6 a cracked gas adsorption film -- desirable -- the above SF 6 considering as the structure which covered the whole mass load induction vibrator containing a cracked gas adsorption film by the fluororesin -- a gas sensor -- SF6 Even when it is left in gas for a long time, sensitivity degradation of a gas sensor can be prevented substantially.

[0009]

[Example] Commercial 9MHzAT cut thickness slipping quartz resonator is explained as mass load induction vibrator as an example of this invention below focusing on the example when using tetrahydro KISHIE chill ethylenediamine (THEED) for gas-adsorption film material. The quartz resonator used for the sensor here has the structure where lead wire 5a and 5b was connected to each drive electrodes 2a and 2b through the conductive pastes 4a and 4b while it forms the drive electrodes 2a and 2b in both sides of the crystal diaphragm 1 and applies the gas-adsorption films 3a and 3b to each drive electrode 2a and 2b upper surface further, as shown in drawing 2 and drawing 3 .

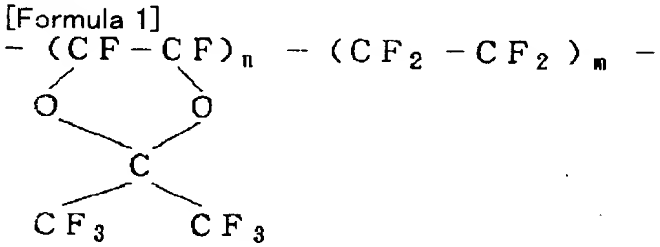
[0010] In addition, the drive electrodes 2a and 2b make a chromium (Cr) layer a ground, and gold (Au) is given. Moreover, lead wire 5a and 5b serves as support of the crystal diaphragm 1 while aiming at connection with an external circuit, and the end face section is being fixed to the insulating susceptor 6.

[0011] It applies so that a frequency shift amount may be set to about 10kHz on drive electrode 2a and 2b in THEED as a gas-adsorption film, acting [as it connects with the oscillator circuit 7 as the gas-adsorption films 3a and 3b indicated the lead wire 5a and 5b of a quartz resonator to be to drawing 4 first in the sensor of this example and is further shown in drawing 5 , connect with an electronic counter 8, and] as the monitor of the oscillation frequency by the electronic counter 8.

[0012] C, F, and O are used as a composition element for the whole vibrator containing these gas-adsorption films 3a and 3b. next, as a meltable fluororesin to a fluorocarbon system solvent For example, the perfluoro (2 and 2-dimethyl -1, 3-JIOKI SOL) amorphous fluororesin (Dupont AF-1600) which consists of a copolymer of a tetrafluoroethylene and a perfluoro JIOKI SOL as shown in the following chemical formula (1) SF6 of structure as dried on condition that a request and created the amorphous fluororesin layer 9, after dipping in the solution which carried out dissolution dilution and taking out, so that it may become desired thickness with a perfluoro solvent (FURORINATO FC75 made from 3M), and shown in drawing 1 It considered as the decomposition gas sensor 10.

[0013]

[Formula 1]



(1)

[0014] Thus, created SF6 Evaluation of a decomposition gas sensor was performed as follows. Namely, SF6 of the above [terminal / seal / 12 / of the proof-pressure hermetically sealed enclosure 11 of 2.5l. of content volume / as shown in drawing 6] The decomposition gas sensor 10 is attached. It drives by the oscillator circuit 7 besides the proof-pressure hermetically sealed enclosure 11, and can be made to carry out in an electronic counter 8 the monitor of the frequency. SF6 after carrying out evacuation of the inside of the proof-pressure hermetically sealed enclosure 11 It is filled up with gas so that it may become one atmospheric pressure from a container 13. SF6 after a request carries out time neglect It is SOF2 as an example of representation of cracked gas. It pours in by the syringe 14 so that it may become desired concentration using gas, and it is SOF2 from the frequency after neglect. Duplicate measurement of the frequency shift amount at the time of insufflation (sensitivity) was carried out, and it was performed. The result of each example of an experiment is explained in detail below.

[0015] First, in order to show the effect of this invention clearly, the property of the sensor which formed only the gas-adsorption film (THEED) as a conventional example is explained. The sensor (equivalent to what is shown in drawing 2 and drawing 3) of the conventional example is attached in the seal terminal 12 of the proof-pressure hermetically sealed enclosure 11 of drawing 6 , and it is SF6 about the inside of the proof-pressure hermetically sealed enclosure 11. The frequency change when filling up and leaving it was measured so that it might become one atmospheric pressure by gas, and the result was shown in drawing 7 . The fall in early stages with the big frequency of a sensor was expected to be clear from drawing 7 , and the change has decreased soon. It is SF6 as mentioned above. Only 24 hours is [the sensor "a" stabilized in neglect among gas, and] SF6. SOF2 of the sensor "b" left among gas Duplicate measurement of the gas sensitivity (frequency shift when setting concentration to 1000 ppm) is carried out, and the result is shown in drawing 8 . SF6 Although the sensor "b" left in gas only for 24 hours showed high sensitivity comparatively by 1st measurement, whenever it repeats measurement, sensitivity is falling. SF6 The sensor "a" stabilized in gas hardly shows sensitivity from the 1st measurement.

[0016] Next, after it dipped the sensor same as an example of this invention as what was created as the former in the solution which carried out concentration adjustment so that the thickness of an amorphous fluororesin (Dupont AF1600) might be set to 0.5 micrometers, and it carried out predrying at the room temperature, actual dryness was carried out for 30 minutes at 80 degrees C, and the sensor (sample 1) of structure like drawing 1 was created. The result which estimated the sensor of a sample 1 as the conventional example similarly is shown in drawing 9 and 10. Drawing 9 is SF6. It is what showed the result of the frequency change when carrying out continuation neglect in gas, and the amount of frequency falls of the sensor (sample 1) which carried out the amorphous fluororesin coat has decreased sharply compared with the conventional example. Moreover, SOF2 similarly shown in drawing 10 The sensitivity fall by the repeat of the measurement of a sensor (sample 1) which carried out the amorphous fluororesin coat to the result of the duplicate measurement by gas has decreased sharply.

[0017] Next, in order to investigate the scope of the thickness of an amorphous fluororesin, the dryness conditions of an amorphous fluororesin were considered as the same room temperature predrying as an example 1, and this dryness for 80 degree-Cx 30 minutes, and the response time and initial sensitivity (SOF2 gas concentration is 200 ppm) of samples 1-6 which changed the thickness to 0.05 to 3 micrometers were measured. The result is shown in Table 1. if thickness becomes thick, although the inclination for the response time to become long will be seen, the change at 0.1 micrometers or more of thickness with not much big sensitivity is seen -- not having -- an average -- the property that about 0.6 ppm per Hz and minute amount concentration change are detectable with resolution is shown However, if it exceeds 2 micrometers, the oscillation of a sensor will become unstable and it will not oscillate in 3 micrometers or more.

[0018]

[Table 1]

非晶質フッ素樹脂の膜厚効果

試料No.	膜厚（μm）	応答時間（分）	初期感度（Hz） SOF_2=200ppm
2	0.05	6	800
3	0.10	5	340
1	0.50	6	320
4	1.00	10	300
5	2.00	15	250
6	3.00	発振せず	発振せず

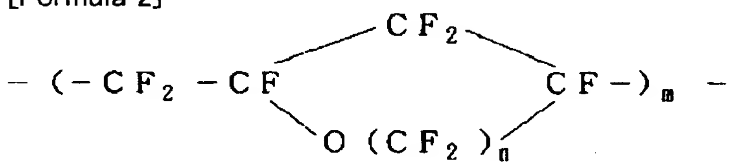
[0019] Drawing 11 and 12 are SF6 about the above-mentioned samples 1-5. The case where it is left inside, and the example which performed repeat measurement of sensitivity (SOF2 gas-concentration 1000pppm) are shown, and like the conventional example, the sensor (sample 2) of 0.05 micrometers of thickness showed high sensitivity in early stages, and showed the inclination for frequency and sensitivity to fall greatly by neglect. In thickness 0.1 micrometers or more, although a response becomes slow with the increase in thickness, the fall of sensitivity is not so large. Although the upper limit of the amorphous fluororesin thickness in this sensor was prescribed by quartz-resonator oscillation conditions (fall of Q (stability index) of the quartz resonator by the amorphous fluororesin coat), the property with this thickness especially good in 0.1 to 1 micrometer was acquired. However, depending on the physical properties of an adsorption film, at least 0.05 micrometers of good properties are acquired.
[0020] Next, the relation between the drying temperature at the time of amorphous fluororesin film formation and the property of a sensor is explained as samples 7-12. In the above-mentioned samples 2-6, although they were performed for 30 minutes at 80 degrees C after carrying out predrying of the dryness conditions after amorphous fluororesin coating at a room temperature, in samples 7-12, they made thickness of gas-adsorption film material and an amorphous fluororesin the same as a sample 1, performed this dryness after coating among 160 degrees C from the room temperature, and investigated it about the surface state of an amorphous fluororesin film, the response time, and sensitivity. The result is shown in Table 2. By the sample 10 whose drying temperature is 140 degrees C, the wrinkling was looked at a little by the film, and the crack has generated the surface state of an amorphous fluororesin film by the samples 11 and 12 higher than it. Moreover, although the difference to nearly 140 degrees C with so big response-time sensitivity about a property was not seen, when it surpasses 160 degrees C, the sensitivity for a crack is large suddenly. 140 degrees C is suitable for the drying temperature when forming amorphous fluororesin AF1600 on the gas-adsorption film THEED from this from a room temperature.
[0021]
[Table 2]

非晶質フッ素樹脂膜乾燥温度の効果

試料No.	乾燥温度 (℃)	膜状態	応答時間 (分)	感度 (Hz) SOF_2=1000ppm
7	室温	良好	6.0	600
1	室温→80	良好	5.5	550
8	室温→100	良好	5.0	500
9	室温→120	良好	4.0	500
10	室温→140	ややしわ	4.5	550
11	室温→160	クラック	5.0	650
12	室温→180	クラック	5.0	750

[0022] In addition, although the effect of this drying temperature is the example which used FURORINATO FC-75 (boiling point of 102 degrees C), and the same property is acquired even if it uses other perfluoro system solvents -113, for example, chlorofluocarbon, FURORINATO (3 M company make), ARURUDO (Asahi Glass make), Galden (Montefluos make), etc., the rate of dilution, dryness conditions, etc. will shift from this result somewhat by the difference in the solvent in this case.
[0023] Next, equipment, i.e., the equipment which connected the electric discharge circuit 15 to the equipment of drawing 6 , in order to show the effectiveness in real cracked gas detection of each sample, as shown in drawing 13 about the sensor of a sample 8 is used, and it is SF6. The result which was made to generate the cracked gas which caused electric discharge in gas 1 atmospheric pressure, and investigated the responsibility is shown in drawing 14 . In addition, 16 show a discharge electrode among this electric discharge circuit 15, and 17 shows high-pressure AC power supply. For the sensor of a sample 8, when it was made to leave it for 30 seconds in 15kVx13mA, about 300Hz frequency fall was seen, subsequent SF6 inert gas replacement has recovered on the original level mostly in about 5 minutes, and the sensor of this invention is SF6. It is shown that it is effective in detection of cracked gas.
[0024] These samples are SF6 about AT-cut thickness slipping quartz resonator as mass load induction vibrator. About THEED, it is Dupont to an amorphous fluororesin film in cracked gas adsorption-film material. Although the example using AF-1600 was explained In others, if a surface wave (SAW) device, a tuning fork vibrator, a ceramic piezoelectric transducer, single crystal silicon, or polycrystal silicon vibrator can output change of a mass load as electrical property change of vibrator as mass load induction vibrator, there will be especially no limit.
[0025] SF6 What is necessary is just the material which is easy to adsorb a sour gas by owner polarity like Triethanolamine, Quadrol, Armeen2S, Amine220, p-Toluidine, Tredodecylamine, Carbowax400, Carbowax20M, and Ethylenedinitrilotetraethanol as a cracked gas adsorption-film material. Moreover, when Asahi Glass SAITOPPU as chosen an amorphous fluororesin not only the thing of the above-mentioned example but well-known as an amorphous fluororesin suitably, for example, shown in AF-2400 of Dupont

and a chemical formula (2) was diluted and used with the exclusive solvent (a tradename is AFURUDO), the same effect as the samples 1-12 of the above-mentioned experiment was acquired.
[0026]
[Formula 2]



(2)

[0027] In addition, in order to perform highly precise detection using the sensor of this invention, the degree-ized meanses of constant temperature, such as a heater and a pay RUCHIE element, are used, and it may be made to make temperature of a sensor regularity. Moreover, how to take differential with the reference sensor which enclosed the sensor with the same property as this sensor with the thermally conductive airtight container from which the capacity changes with change of external pressure with the standard gas, and the method of containing in memory the thermal stress property measured beforehand, and compensating a property based on temperature and pressure information are also considered.
[0028]
[Effect of the Invention] As explained above, according to this invention, mass load induction vibrator at least to a mass load induction side SF6 A cracked gas adsorption film is formed and a gas sensor with little sensitivity degradation can be realized by making it the structure which covered at least the above-mentioned gas-adsorption film and the whole mass load induction vibrator which contains the above-mentioned gas-adsorption film more preferably by the fluororesin. It is SF6 by using this. SF6 in a gas-charging electrical machinery and apparatus Cracked gas is detectable on high sensitivity and a continuation target. In addition, the sensor of this invention is SF6. It is applicable also to the of-the-same-kind type sensor of an except.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The quartz-resonator type gas sensor concerning this invention is a cross section a part.
[Drawing 2] Front view of a quartz-resonator type gas sensor.
[Drawing 3] The side elevation of a quartz-resonator type gas sensor shown in drawing 2 .
[Drawing 4] The oscillator-circuit view of a quartz-resonator type gas sensor.
[Drawing 5] The side elevation of the coverage monitoring device of a gas-adsorption film.
[Drawing 6] SF6 ** type view of cracked gas response characteristic evaluation equipment.
[Drawing 7] SF6 of the conventional example Diagram showing a neglect-among gas result.
[Drawing 8] SF6 of the conventional example Diagram showing gas (1000 ppm of cracked gas) sensitivity change.
[Drawing 9] SF6 of a sample 1 Diagram showing a neglect-among gas result.
[Drawing 10] SF6 of a sample 1 Diagram showing gas (1000 ppm of cracked gas) sensitivity change.
[Drawing 11] SF6 of examples 1-5 Diagram showing a neglect-among gas result.
[Drawing 12] SF6 of examples 1-5 Diagram showing gas (1000 ppm of cracked gas) sensitivity change.
[Drawing 13] The ** type view of electric discharge cracked gas response characteristic evaluation equipment.
[Drawing 14] SF6 of an example 8 Diagram showing an electric discharge cracked gas response characteristic.
[Description of Notations]
1 [-- A gas-adsorption film, 4a, 4b / -- An electric conduction paste,, 5a, 5b / -- A lead-wire insulation, 6 / -- A susceptor, 7 / -- An oscillator circuit, 8 / -- An electronic counter, 9 / -- An amorphous fluororesin, 10 / -- SF6 / A decomposition gas sensor, 11 / -- SF6 / -- A proof-pressure hermetically sealed enclosure, 12 -- A seal terminal, 13] -- A quartz plate, 2a, 2b -- A drive electrode, 3a

[Translation done.]

* NOTICES *

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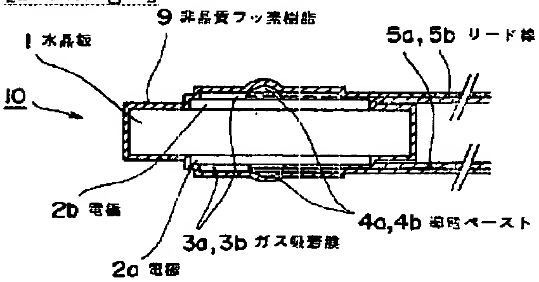
1.This document has been translated by computer. So the translation may not reflect the original precisely.

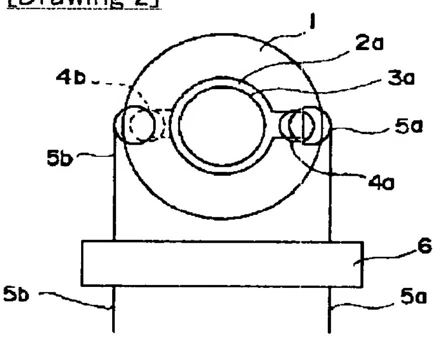
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

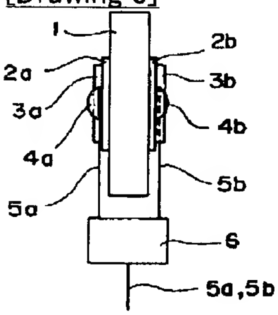
[Drawing 1]



[Drawing 2]



[Drawing 3]



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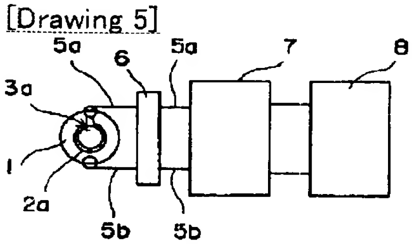

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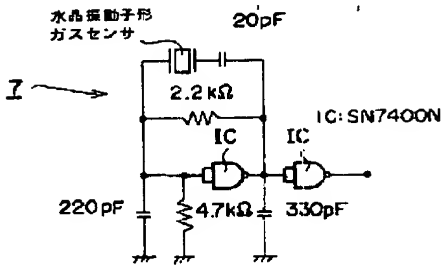
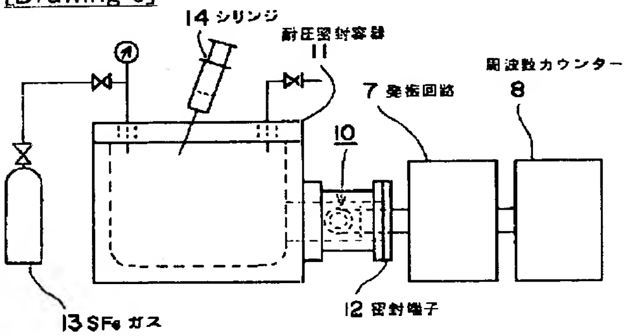
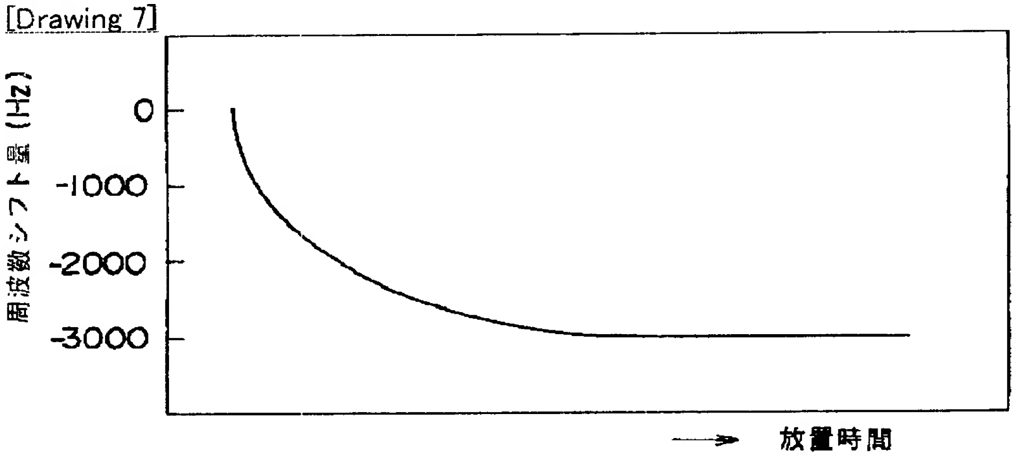


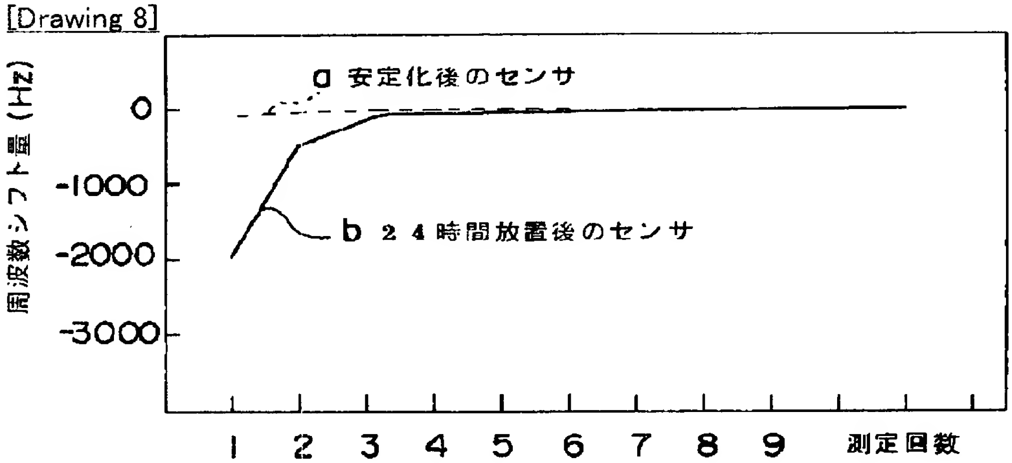
[Drawing 6]



[Drawing 7]



[Drawing 8]



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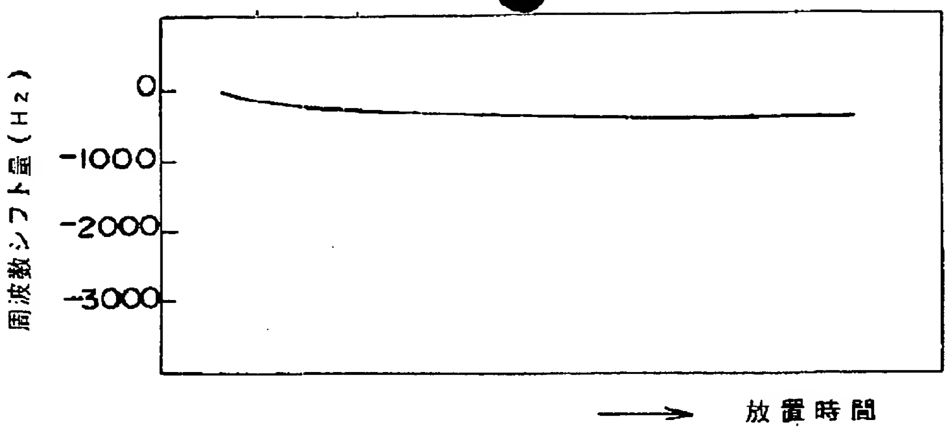
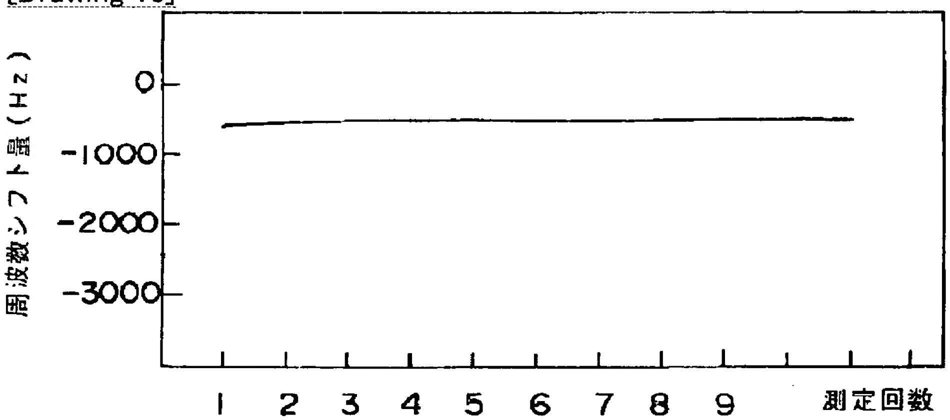
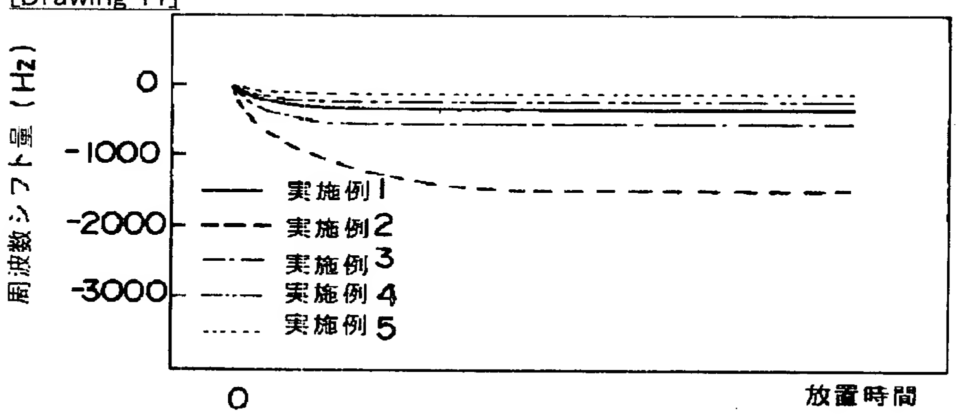


[Drawing 10]



[Drawing 11]



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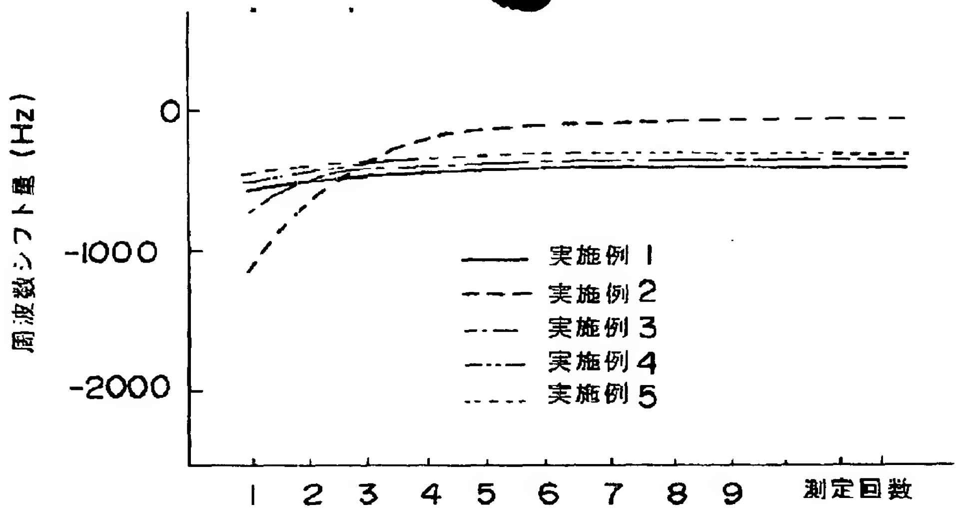
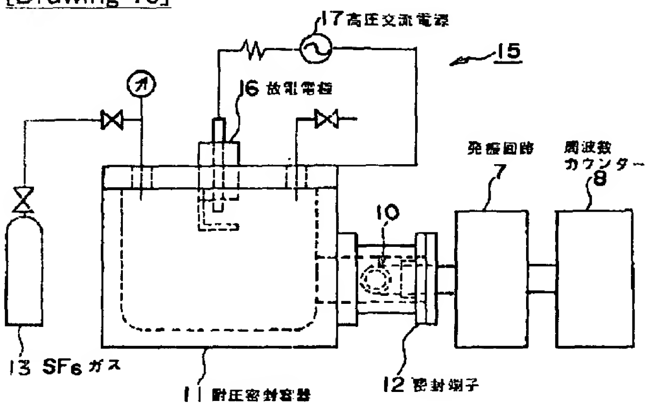
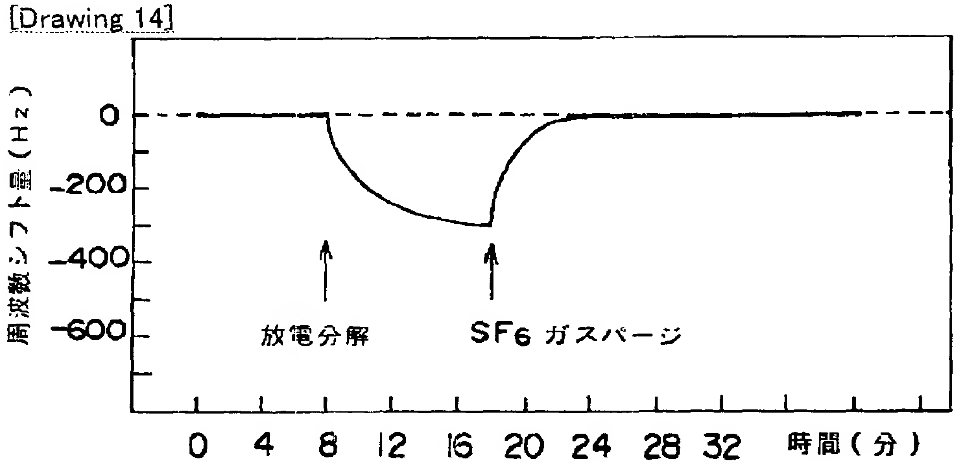


[Drawing 13]



[Drawing 14]



[Translation done.]

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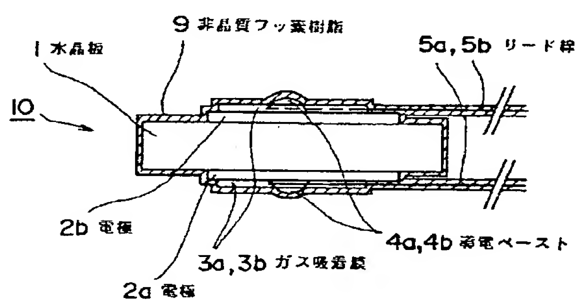
(54)【発明の名称】　六フッ化硫黄分解ガスセンサ

(57)【要約】

【目的】　本発明は、感度劣化の少ないＳＦ$_6$分解ガスセンサの提供を目的とする。

【構成】　質量負荷感応振動子の質量負荷感応面にＳＦ$_6$分解ガス吸着膜を形成し、ＳＦ$_6$分解ガス吸着膜、好ましくはＳＦ$_6$分解ガス吸着膜を含む質量負荷感応振動子全体をフッ素樹脂で覆った構造からなることを特徴とする。

【効果】　フッ素樹脂で覆った構造にすることにより、ＳＦ$_6$ガスおよびＳＦ$_6$分解ガスに対して感度劣化の少ないセンサが実現でき、これを用いることによりＳＦ$_6$ガス封入電気機器内のＳＦ$_6$分解ガスを高感度で、かつ長期間連続して検出できる。



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【特許請求の範囲】

【請求項１】　質量負荷の変化に感応してその電気特性が変化する質量負荷感応振動子の少なくとも質量負荷感応面に形成された六フッ化硫黄分解ガス吸着膜と、少なくとも上記ＳＦ$_6$分解ガス吸着膜を被覆するフッ素樹脂層とを具備してなることを特徴とする振動子型六フッ化硫黄解ガスセンサ。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、例えば高電圧用電気機器に絶縁ガスとして封入されている六フッ化硫黄（ＳＦ$_6$）の分解ガスを検出するための振動子型ＳＦ$_6$分解ガスセンサに関する。

【０００２】

【従来の技術】高電圧、高電流を取扱う電気機器の絶縁ガスとして一般的にＳＦ$_6$が用いられている。これは、ＳＦ$_6$ガスの持つ熱的、化学的安定性によるものである。しかし、ＳＦ$_6$が封入された電気機器内部に酸素や水分が存在し、コロナ放電やアーク放電が起こると、これら酸素や水分の介在によりＳＯＦ$_2$，ＳＯ$_2$Ｆ$_2$等の低級フッ化硫黄ガスやＨＦガス等のＳＦ$_6$分解ガスを生じる。これらの分解ガスは酸性の腐食ガスであり電気機器の絶縁性低下の原因となるため、低濃度の段階において絶縁ガスの異常を検知する必要がある。このため、例えばガス絶縁開閉装置（以下、ＧＩＳと略称する）に於いては、ガスクロマトグラフを用いる方法（電気協同研究第３３巻第４号、ＳＦ$_6$絶縁機器保守基準参照）や、呈色反応試薬を用いたガスチェッカー（三菱電機技報Ｖｏｌ．６０・Ｎｏ６・１９８６）等が用いられている。しかしながら、これ等の装置を用いた測定は極めて手間と時間が掛かる作業であるため、ＳＦ$_6$分解ガスの検出を自動化するための高感度で連続検出可能なセンサの開発が望まれている。

【０００３】一方、近年ガスセンサの分野において高感度で室温駆動可能なガスセンサとして、水晶振動子の質量負荷効果を応用したセンサが数多く試みられている。このセンサは一般に水晶振動子の電極上（質量負荷感応面）にガス吸着膜を形成した構造となっており、ガスの吸着にもとづくガス吸着膜の重量変化Δｗを、下記数式（１）のような原理式で与えられる水晶振動子の発振周波数変化Δｆを測定することによりガスの量が検出できる。

$$\Delta f = -2.3\times10^{6}\times f^{2}\times\Delta w/A \qquad (1)$$

ここで、ｆは水晶振動子の発振周波数、Ａは水晶振動子の電極面積である。

【０００４】ＳＦ$_6$分解ガスセンサとして水晶振動子型ガスセンサをもとに分解ガス吸着材料を種々検討したところ、トリエタノールアミン、クアドロール、テトラハイドロキシエチルエチレンジアミンなどのごとき極性の大きな有機材料がＳＦ$_6$の分解ガスに高感度を示すこと

2

を見出したが、これらの材料をガス吸着膜として形成したセンサをＳＦ$_6$ガス中に放置するセンサの発振周波数は時間とともに低下し安定化する傾向が有り、これにともなってＳＦ$_6$分解ガス感度は短期放置では初期的に感度を示すがやがてほとんどなくなり、ＳＦ$_6$ガス中放置で安定化した後でほとんど感度を示さないという問題点があった。

【０００５】

【発明が解決しようとする課題】本発明は上記事情に鑑みてなされたものであって、ＳＦ$_6$分解ガスを、高感度かつ連続的に検出できるＳＦ$_6$分解ガスセンサを提供することを目的とする。

【０００６】

【課題を解決するための手段】本発明に上記課題を解決するため、質量負荷感応振動子の質量負荷感応面にＳＦ$_6$分解ガス吸着膜を形成するとともに、少なくとも前記ＳＦ$_6$分解ガス吸着膜、好ましくは前記ＳＦ$_6$分解ガス吸着膜を含む質量負荷感応振動子全体をフッ素樹脂で覆うという手段を講じたことを特徴とする。

【０００７】すなわち、本発明は、質量負荷の変化に感応してその電気特性が変化する質量負荷感応振動子の少なくとも質量負荷感応面に形成されたＳＦ$_6$分解ガス吸着膜と、少なくとも上記ＳＦ$_6$分解ガス吸着膜を被覆するフッ素樹脂層とを具備してなることを特徴とする振動子型ＳＦ$_6$分解ガスセンサを提供するものである。

【０００８】

【作用】少なくとも前記ＳＦ$_6$分解ガス吸着膜、好ましくは前記ＳＦ$_6$分解ガス吸着膜を含む質量負荷感応振動子全体をフッ素樹脂で覆った構造とすることにより、ガスセンサをＳＦ$_6$ガス中に長時間放置した場合でもガスセンサの感度劣化を実質的に防止することができる。

【０００９】

【実施例】以下に本発明の実施例として、質量負荷感応振動子として市販の９ＭＨｚＡＴカット厚み滑り水晶振動子を、ガス吸着膜材料にテトラハイドロキシエチルエチレンジアミン（ＴＨＥＥＤ）を用いたときの例を中心に説明する。ここでセンサに使用した水晶振動子は図２および図３に示したように、水晶振動板１の両面に駆動電極２ａ，２ｂを設け、さらに各駆動電極２ａ，２ｂ上面にガス吸着膜３ａ、３ｂを塗布するとともに、各駆動電極２ａ，２ｂに導電性ペースト４ａ，４ｂを介してリード線５ａ，５ｂを接続させた構造となっている。

【００１０】なお、駆動電極２ａ，２ｂはクロム（Ｃｒ）層を下地にして金（Ａｕ）が施されている。また、リード線５ａ，５ｂは外部回路への接続を図るとともに水晶振動板１の支持を兼ねており、その基端部が絶縁性支持台６に固定されている。

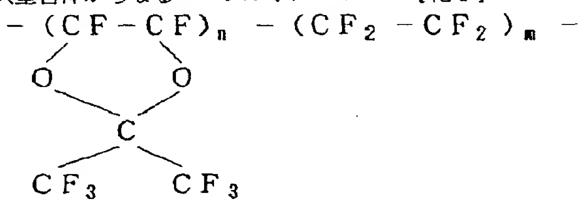
【００１１】この実施例のセンサにおいて、ガス吸着膜３ａ、３ｂは、まず水晶振動子のリード線５ａ，５ｂを図４に示したような発振回路７に接続し、さらに図５に

示すように周波数カウンター８に接続し、周波数カウンター８で発振周波数をモニターしながら、ガス吸着膜としてＴＨＥＥＤを駆動電極２ａ，２ｂ上に周波数シフト量が１０ＫＨｚ程度になるように塗布したものである。

【００１２】次に、このガス吸着膜３ａ、３ｂを含む振動子全体を、Ｃ、Ｆ、Ｏを構成元素とし、フロロカーボン系溶媒に可溶なフッ素樹脂として、例えば下記化学式（１）に示したようなテトラフルオロエチレンとパーフルオロジオキソールの共重合体からなるパーフルオロ＊（２，２－ジメチル－１，３－ジオキソール）非晶質フッ素樹脂（Ｄｕｐｏｎｔ　ＡＦ－１６００）をパーフルオロ溶媒（３Ｍ製フロリナートＦＣ７５）で所望の膜厚になるように溶解希釈した溶液に浸し、取り出した後、所望の条件で乾燥させて非晶質フッ素樹脂層９を作成し、図１に示すような構造のSF_6分解ガスセンサ１０とした。

【００１３】

【化１】



（１）

【００１４】このようにして作成したSF_6分解ガスセンサの評価を以下のようにして行った。すなわち、図６に示したような内容積２．５ｌの耐圧密封容器１１の密封端子１２に上記のSF_6分解ガスセンサ１０を取付け、耐圧密封容器１１外の発振回路７により駆動され、周波数カウンター８にて周波数をモニターできるようにし、耐圧密封容器１１内を真空排気した後、SF_6ガスを容器１３から１気圧になるように充填し、所望の時間放置した後、SF_6の分解ガスの代表例としてSOF_2ガスを用いて所望の濃度となるようにシリンジ１４で注入し、放置後の周波数からのSOF_2ガス注入時の周波数シフト量（感度）を繰返し測定して行った。以下に各実験例の結果を詳細に説明する。

【００１５】まず、本発明の効果を明確に示すため、従来例としてガス吸着膜（ＴＨＥＥＤ）のみを形成したセンサの特性を説明する。従来例のセンサ（図２、図３に示すものに相当）を図６の耐圧密封容器１１の密封端子１２に取り付け、耐圧密封容器１１内をSF_6ガスで１気圧となるように充填し放置したときの周波数変化を測定し、その結果を図７に示した。図７から明らかなようにセンサの周波数は初期に大きな低下がみられ、やがてその変化は少なくなっている。上述のようにSF_6ガス中放置で安定させたセンサ“ａ”と２４時間だけSF_6ガス中放置したセンサ“ｂ”の、SOF_2ガス感度（濃度を１０００ｐｐｍにした時の周波数シフト）を繰返し測定し、その結果を図８に示す。SF_6ガス中で２４時間だけ放置したセンサ“ｂ”は、１回目の測定で比較的高感度を示したが、測定を重ねるごとに感度が低下している。SF_6ガス中で安定化させたセンサ“ａ”は、１回目の測定からほとんど感度を示さない。

【００１６】次に本発明の実施例として、従来として作成したものと同じセンサを、非晶質フッ素樹脂（Ｄｕｐｏｎｔ　ＡＦ１６００）の膜厚が０．５μｍとなるように濃度調整した溶液に浸し、室温で予備乾燥した後、８０℃で３０分間本乾燥し図１のような構造のセンサ（試料１）を作成した。試料１のセンサを従来例と同様に評価した結果を図９，１０に示す。図９はSF_6ガス中で連続放置したときの周波数変化の結果を示したもので、非晶質フッ素樹脂コートしたセンサ（試料１）は従来例に比べ周波数低下量が大幅に少なくなっている。また同様に図１０に示したSOF_2ガスによる繰返し測定の結果においても、非晶質フッ素樹脂コートしたセンサ（試料１）の測定の繰り返しによる感度低下は大幅に少なくなっている。

【００１７】次に非晶質フッ素樹脂の膜厚の有効範囲を調べるため、非晶質フッ素樹脂の乾燥条件を実施例１と同じ室温予備乾燥と８０℃×３０分の本乾燥とし、その膜厚を０．０５から３μｍまで変えた試料１～６の応答時間と初期感度（SOF_2ガス濃度は２００ｐｐｍ）を測定した。その結果を表１に示す。膜厚が厚くなると応答時間が長くなる傾向が見られるものの、感度は膜厚０．１μｍ以上であまり大きな変化は見られず平均分解能で１Ｈｚ当たり約０．６ｐｐｍと微量濃度変化を検出できる特性を示している。しかし２μｍを超えるとセンサの発振が不安定となり、３μｍ以上では発振しない。

【００１８】

【表１】

非晶質フッ素樹脂の膜厚効果

試料No	膜厚（μm）	応答時間（分）	初期感度（Hz）SOF_2=200ppm
2	0.05	6	800
3	0.10	5	340
1	0.50	6	320
4	1.00	10	300
5	2.00	15	250
6	3.00	発振せず	発振せず

【0019】図11，12は上記試料1～5をSF_6中放置した場合と、感度（SOF_2ガス濃度1000ppm）の繰り返し測定を行った例を示すものであり、膜厚0．05μmのセンサ（試料2）は従来例のように、初期に高感度を示し、放置により周波数と感度が大きく低下する傾向を示した。0．1μm以上の膜厚に於いては、膜厚増加とともに応答が遅くなるものの感度の低下はそれ程大きくない。本センサでの非晶質フッ素樹脂膜厚の上限は水晶振動子発振条件（非晶質フッ素樹脂コートによる水晶振動子のQ（安定度指数）の低下）により規定されるが、この膜厚が0．1μmから1μmの範囲で特に良好な特性が得られた。但し、吸着膜の物性によっては0．05μmでも良好な特性が得られる。

【0020】次に試料7～12として非晶質フッ素樹脂膜形成時の乾燥温度とセンサの特性との関係を説明する。上記試料2～6において、非晶質フッ素樹脂コーティング後の乾燥条件は室温で予備乾燥した後、80℃で30分間行ったが、試料7～12においては、ガス吸着膜材料、非晶質フッ素樹脂の膜厚を試料1と同じにし、コーティング後の本乾燥を室温から160℃の間でおこない、非晶質フッ素樹脂膜の表面状態、応答時間、感度について調べた。その結果を表2に示す。非晶質フッ素樹脂膜の表面状態は、乾燥温度が140℃の試料10では膜にややしわが見られ、それより高い試料11，12ではクラックが発生している。また特性に関しては、応答時間感度とも140℃近辺までそれほど大きな差はみられないが、160℃をこえた場合にはクラックの為か感度が急に大きくなっている。このことからガス吸着膜THEED上に非晶質フッ素樹脂AF1600を形成するときの乾燥温度は室温から140℃が適当である。

【0021】

【表2】

非晶質フッ素樹脂膜乾燥温度の効果

試料No	乾燥温度（℃）	膜状態	応答時間（分）	感度（Hｚ）SOF_2=1000ppm
7	室温	良好	6.0	600
1	室温→80	良好	5.5	550
8	室温→100	良好	5.0	500
9	室温→120	良好	4.0	500
10	室温→140	ややしわ	4.5	550
11	室温→160	クラック	5.0	650
12	室温→180	クラック	5.0	750

【0022】尚、この乾燥温度の効果はフロリナートＦＣ－７５（沸点１０２℃）を用いた例で、他のパーフルオロ系溶媒、例えばフロン－１１３、フロリナート（３M社製）、アルルード（旭硝子製）、ガルデン（モンテフルオス社製）などを用いても同様な特性が得られるが、この場合はその溶媒の違いにより稀釈率、乾燥条件などが今回の結果と多少ずれることになる。

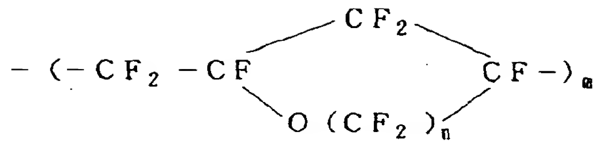
【００２３】次に各試料の実分解ガス検出における有効性を示すため、試料８のセンサについて、図１３に示したような装置、すなわち、図６の装置に対して放電回路１５を接続した装置を用いてSF_6ガス１気圧中で放電を起こした分解ガスを発生させその応答性を調べた結果を図１４に示す。なお、この放電回路１５中、１６は放電電極、１７は高圧交流電源を示す。試料８のセンサは、１５ＫＶ×１３ｍＡで３０秒間放置させたとき約３００Ｈｚの周波数低下がみられ、その後のSF_6ガス置換により約５分間でほぼ元のレベルに回復しており、本発明のセンサがSF_6分解ガスの検出に有効であることを示している。

【００２４】それら試料は、質量負荷感応振動子としてＡＴ－カット厚み滑り水晶振動子を、SF_6分解ガス吸着膜材料にＴＨＥＥＤを、非晶質フッ素樹脂膜にＤｕｐｏｎｔ　ＡＦ－１６００を用いた例を説明したが、他に質量負荷感応振動子としては表面波（ＳＡＷ）デバイス、音叉振動子、セラミック圧電振動子、単結晶シリコンまたは多結晶シリコン振動子等、質量負荷の変化を振動子の電気特性変化として出力できるものであれば特に制限はない。

【００２５】SF_6分解ガス吸着膜材料としてはＴｒｉｅｔｈａｎｏｌａｍｉｎｅ，Ｑｕａｄｒｏｌ，Ａｒｍｅｅｎ２Ｓ，Ａｍｉｎｅ２２０，ｐ－Ｔｏｌｕｉｄｉｎｅ，Ｔｒｅｄｏｄｅｃｙｌａｍｉｎｅ，Ｃａｒｂｏｗａｘ４００，Ｃａｒｂｏｗａｘ２０Ｍ，Ｅｔｈｙｌｅｎｅｄｉｎｉｔｒｉｌｏｔｅｔｒａｅｔｈａｎｏｌ等のように有極性で酸性ガスを吸着しやすい材料であればよい。また非晶質フッ素樹脂としても上記例のものに限らず、公知の非晶質フッ素樹脂を適宜選択することができ、例えばＤｕｐｏｎｔのＡＦ－２４００、化学式（２）に示すような旭硝子製サイトップをその専用溶媒（商品名はアフルード）で希釈して用いた場合においても、上記実験の試料１から１２と同様な効果が得られた。

【００２６】

【化２】


（２）

【００２７】なお、本発明のセンサを用いて高精度な検出を行うために、ヒーターやペルチェ素子等の定温度化手段を用いて、センサの温度を一定にするようにしてもよい。また、本センサと同一の特性を持つセンサを、外圧の変化によりその容積が変化する熱伝導性の密閉容器に標準ガスとともに封入した参照センサとの差動をとる方法や、予め測定された温度圧力特性をメモリーに収納し、温度、圧力情報をもとに特性を補償する方法も考えられる。

【００２８】

【発明の効果】以上説明した様に本発明によれば、質量負荷感応振動子の少なくとも質量負荷感応面に、SF_6分解ガス吸着膜を形成し、少なくとも上記ガス吸着膜、より好ましくは上記ガス吸着膜を含む質量負荷感応振動子全体をフッ素樹脂で覆った構造にすることにより感度劣化の少ないガスセンサが実現でき、これを用いることによりSF_6ガス封入電気機器内のSF_6分解ガスを高感度かつ連続的に検出することができる。なお、本発明のセンサはSF_6以外の同種タイプのセンサにも適用できる。

【図面の簡単な説明】

【図１】本発明に係わる水晶振動子型ガスセンサの一部断面図。

【図２】水晶振動子型ガスセンサの正面図。

【図３】図２に示す水晶振動子型ガスセンサの側面図。＊

＊【図４】水晶振動子型ガスセンサの発振回路図。

【図５】ガス吸着膜の塗布量モニタ装置の側面図。

【図６】ＳＦ６分解ガス応答特性評価装置の模式図。

【図７】従来例のSF_6ガス中放置結果を示す線図。

【図８】従来例のSF_6ガス（分解ガス１０００ｐｐｍ）感度変化を示す線図。

【図９】試料１のSF_6ガス中放置結果を示す線図。

【図１０】試料１のSF_6ガス（分解ガス１０００ｐｐｍ）感度変化を示す線図。

【図１１】実施例１～５のSF_6ガス中放置結果を示す線図。

【図１２】実施例１～５のSF_6ガス（分解ガス１０００ｐｐｍ）感度変化を示す線図。

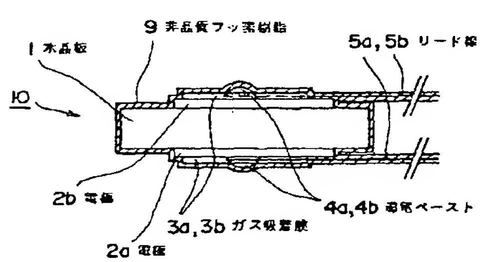
【図１３】放電分解ガス応答特性評価装置の模式図。

【図１４】実施例8のSF_6放電分解ガス応答特性を示す線図。

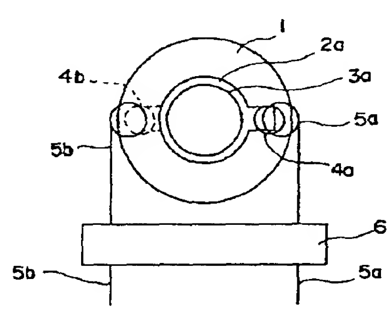
【符号の説明】

１…水晶板、２ａ、２ｂ…駆動電極、３ａ、３ｂ…ガス吸着膜、４ａ、４ｂ…導電ペースト、５ａ、５ｂ…リード線絶縁、６…支持台、７…発振回路、８…周波数カウンター、９…非晶質フッ素樹脂、１０…SF_6分解ガスセンサ、１１…耐圧密封容器、１２…密封端子、１３…SF_6ガス容器、１４…シリンジ、１６…放電電極、１７…交流高圧電源。

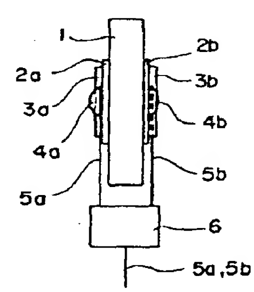
【図１】



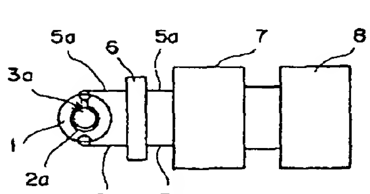
【図２】



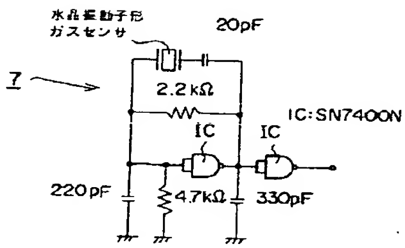
【図３】



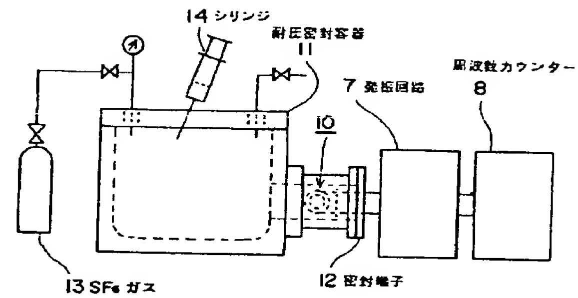
【図５】



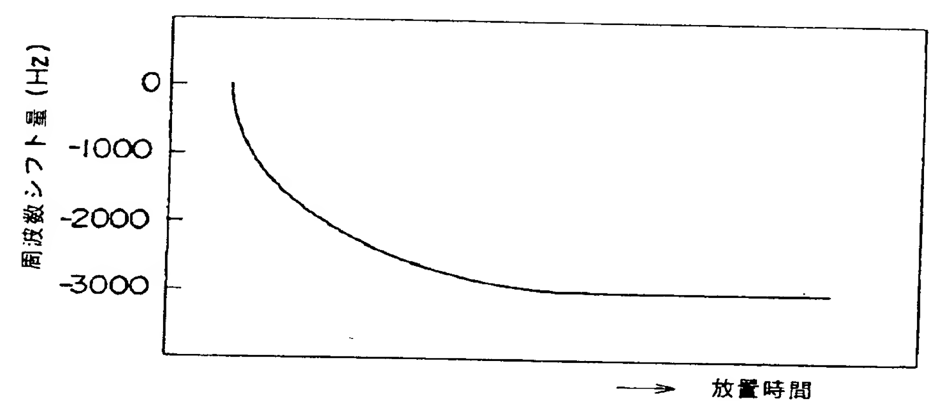
【図4】


水晶振動子形
ガスセンサ
20pF
7
2.2kΩ
IC:SN7400N
IC
IC
220pF
4.7kΩ
330pF

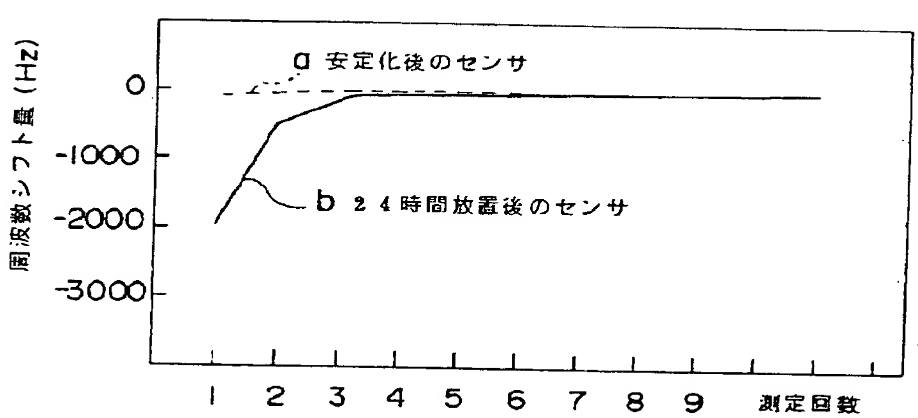
【図6】


14 シリンジ
耐圧密封容器
11
7 発振回路
周波数カウンター
8
10
13 SFe ガス
12 密封端子

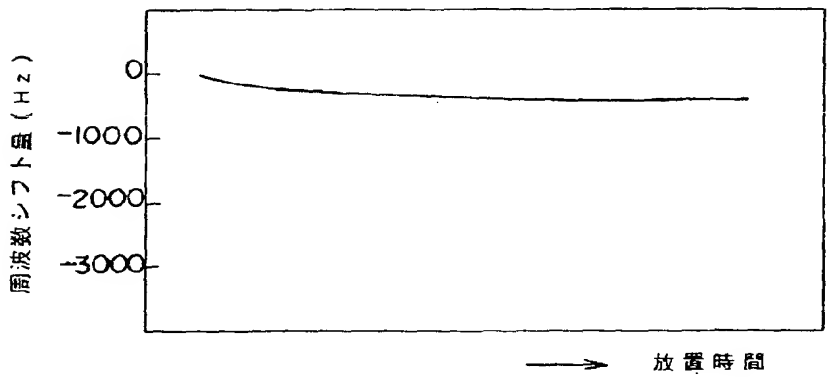
【図7】


周波数シフト量 (Hz)
0
-1000
-2000
-3000
放置時間

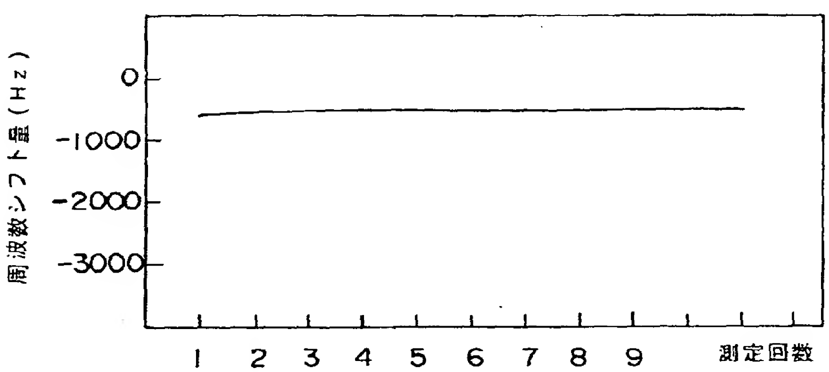
【図8】


周波数シフト量 (Hz)
0
-1000
-2000
-3000
a 安定化後のセンサ
b 24時間放置後のセンサ
1
2
3
4
5
6
7
8
9
測定回数

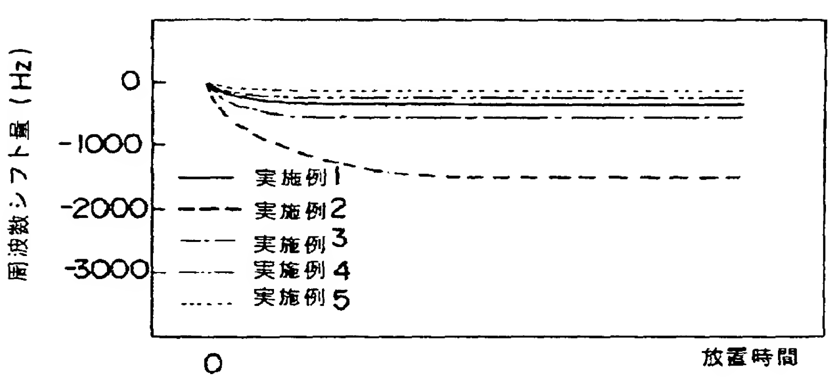
【図9】


周波数シフト量（Hz）
0
-1000
-2000
-3000
放置時間

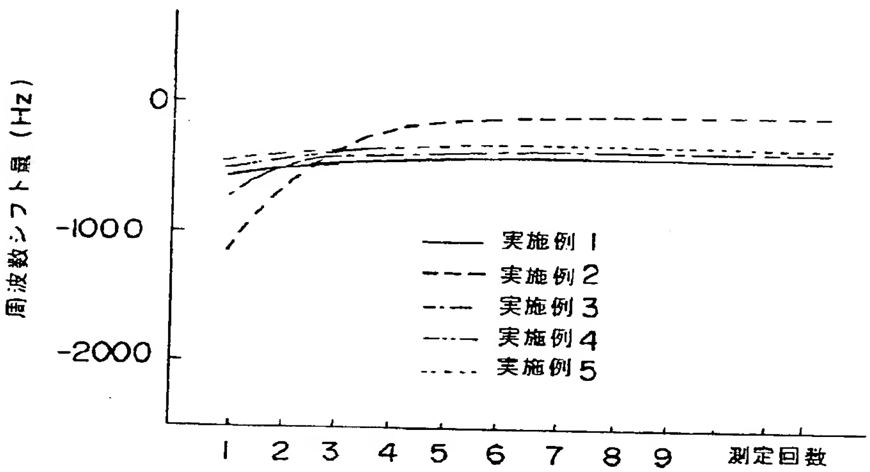
【図10】


周波数シフト量（Hz）
0
-1000
-2000
-3000
1
2
3
4
5
6
7
8
9
測定回数

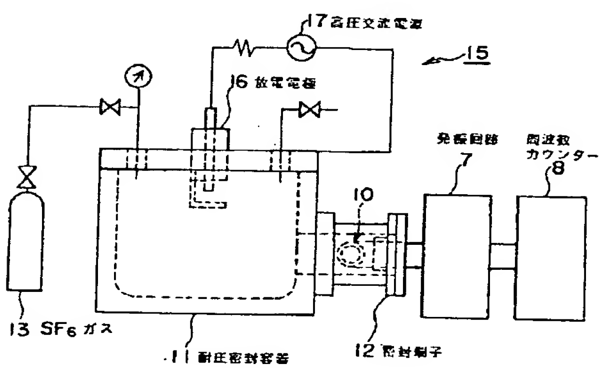
【図11】


周波数シフト量（Hz）
0
-1000
-2000
-3000
実施例1
実施例2
実施例3
実施例4
実施例5
0
放置時間

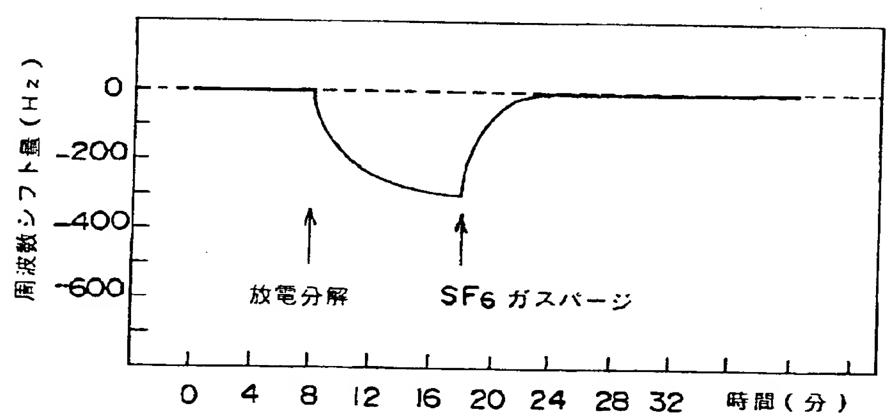
【図12】


0
-1000
-2000
周波数シフト量 (Hz)
実施例 1
実施例 2
実施例 3
実施例 4
実施例 5
1 2 3 4 5 6 7 8 9
測定回数

【図13】


17 高圧交流電源
15
16 放電電極
発振回路
7
周波数
カウンター
8
10
13 SF6 ガス
11 耐圧密封容器
12 密封端子

【図14】


0
-200
-400
-600
周波数シフト量 (Hz)
放電分解
SF6 ガスパージ
0 4 8 12 16 20 24 28 32
時間 (分)